PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference	FOR FURTHER ACTION	see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.
99371		
International application No.	International filing date *(day/month/year)*	(Earliest) Priority Date *(day/month/year)*
PCT/IL 00/ 00588	21/09/2000	23/09/1999
Applicant		
CHEMERGY LTD. et al.		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 2 sheets.

[X] It is also accompanied by a copy of each prior art document cited in this report.

1. **Basis of the report**
   a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.
      [ ] the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).
   b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing :
      [ ] contained in the international application in written form.
      [ ] filed together with the international application in computer readable form.
      [ ] furnished subsequently to this Authority in written form.
      [ ] furnished subsequently to this Authority in computer readble form.
      [ ] the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
      [ ] the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. [ ] **Certain claims were found unsearchable** (See Box I).

3. [ ] **Unity of invention is lacking** (see Box II).

4. With regard to the **title,**
   [X] the text is approved as submitted by the applicant.
   [ ] the text has been established by this Authority to read as follows:

5. With regard to the **abstract,**
   [X] the text is approved as submitted by the applicant.
   [ ] the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No. ______
   [ ] as suggested by the applicant.
   [ ] because the applicant failed to suggest a figure.
   [ ] because this figure better characterizes the invention.
   [X] None of the figures.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/[illegible]00/00588

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C25B1/28 H01M4/58

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C25B H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 217 584 A (J. PAUL DEININGER) 8 June 1993 (1993-06-08) column 15 -column 18; example 3 ---	1,2,5,9, 10,22, 23,27,29
X	WO 98 50970 A (CHEMERGY LTD) 12 November 1998 (1998-11-12) see whole document -----	1,2, 5-12, 15-17, 20-35,37

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier document but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
26 February 2001	06/03/2001

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Groseiller, P

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/[illegible]00/00588

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5217584 A	08-06-1993	AU 8919991 A	20-05-1992
		WO 9207114 A	30-04-1992
WO 9850970 A	12-11-1998	AU 729009 B	25-01-2001
		AU 7077298 A	27-11-1998
		BR 9809231 A	31-10-2000
		CN 1260069 T	12-07-2000
		EP 0974169 A	26-01-2000
		PL 336666 A	03-07-2000
		US 6033343 A	07-03-2000

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PATENT COOPERATION TREATY

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INTERNATIONAL PRELIMINARY EXAMINATION REPORT

12

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference 99371	FOR FURTHER ACTION	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
International application No. PCT/IL00/00588	International filing date *(day/month/year)* 21/09/2000	Priority date *(day/month/year)* 23/09/1999
International Patent Classification (IPC) or national classification and IPC C25B1/28		
Applicant CHEMERGY LTD. et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 10 sheets, including this cover sheet.

   ☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

   These annexes consist of a total of 15 sheets.

3. This report contains indications relating to the following items:

   I ☒ Basis of the report
   II ☐ Priority
   III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
   IV ☐ Lack of unity of invention
   V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations suporting such statement
   VI ☐ Certain documents cited
   VII ☒ Certain defects in the international application
   VIII ☒ Certain observations on the international application

Date of submission of the demand 28/03/2001	Date of completion of this report 17.01.2002
Name and mailing address of the international preliminary examining authority: European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer Hintermaier, F Telephone No. +49 89 2399 7063

I. Basis of the report

1. With regard to the **elements** of the international application *(Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17))*:

Description, pages:

2,3,5,6,8-11,14, 15,17-19	as originally filed			
1,4,7,12,13,16	as received on	05/12/2001	with letter of	02/12/2001

Claims, No.:

1-44	as received on	05/12/2001	with letter of	02/12/2001

Drawings, sheets:

1/1	as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:
- ☐ the drawings, sheets:

5. ☒ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

   (Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)
   see separate sheet

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	14 - 19, 30 - 44
	No:	Claims	1 - 13, 20 - 29
Inventive step (IS)	Yes:	Claims	14
	No:	Claims	15 - 19, 30 - 44
Industrial applicability (IA)	Yes:	Claims	1 - 44
	No:	Claims	

2. Citations and explanations
   see separate sheet

VII. Certain defects in the international application

The following defects in the form or contents of the international application have been noted:
see separate sheet

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:
see separate sheet

Re Item I
Basis of the report

1. Amended pages 4 and 16 and amended claims 12, 13, 14, 16, 20 and 21 have not been taken into account, since the amendments go beyond the disclosure as filed and hence violate Article 34.2.b PCT.

1.1. The amendment made on page 4, line 17, of the description by inserting "as prepared from the starting anode, cathode and neutral ionic conductor material" goes beyond the description as originally filed, because no part of the cathode material is disclosed in the original description as being transformed into the final Fe(VI) salt. Moreover, this would also contravene the preferred embodiment in which a separator is used in order to avoid material exchange between the cathode cell and the anode cell.

1.2. Page 16:
a) The unit "kg" has been amended to "kg per 1x5 cm^2". However, he introduction of a certain surface area of 1x5 cm^2 goes beyond the disclosure as filed.
b) In line 20 the amount of electrolyte has been changed from 0.32 grams to 0.3 grams.

1.3. Claims 12 - 14, 16 - 21:
The replacement of the word "dissolved" by "mixed" is not allowable, because the meaning of both words are quite different. The original term "dissolved" was considered to be clear.

Re Item V
Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

2. Novelty (Article 33(2) PCT).

Subject-matter of claims 1 -13 and 20 - 29 is not novel for the following reasons:

2.1. Document D1 (WO 98 50970 A) discloses a rechargeable battery comprising two half-cells, which are in electrochemical contact with each other through an electrically

neutral ionic conductor. One of these cells comprises a cathode in form of a **solid Fe(VI) salt** in an amount of at least 1% of the half-cell weight (claim 1). During discharge of the battery the Fe(VI) is reduced to lower oxidation states (claim 1), e.g. to the oxidation state +3 (page 3, line 8). Since the battery is rechargeable (claim 28 and page 6, line 10-13, and example 5), this means that also Fe from a lower oxidation state, e.g. +3, can be oxidised to an Fe(VI) salt. Rechargability here means that the redox reaction can be reversed. Hence, this battery assembly could and would also be used by somebody skilled in the art to produce Fe(VI) salts starting from Fe in lower oxidation states, such as +3. Claims 1 and 2 lack therefore novelty.
Further, the Fe(VI) salt is reduced during discharge in alkaline conditions to FeO(OH) (equation 7, page 14), which means that if the cell is reversed FeO(OH) will be the starting compound for oxidation into the Fe(VI) salt. The ionic conductor can be an aqueous or a non-aqueous solution, a conductive polymer, a molten salt or a solid ionic conductor and can contain a dissolved liquid (claims 8 - 13). The aqueous solution can contain a dissolved Fe(VI) salt (claim 14). The Fe(VI) salt of the cathode can be in contact with a conductive material, which can be graphite, carbon black, a metal or a mixed pressed powder, and which comprises a planar surface or wire or a porous substrate or grid (claims 15 - 19). In addition, also the Fe(VI) compound can be a powder, i.e. be in a solid form, which can be pressed with conductive materials, such as graphite or carbon black (page 5, line 4 - 6). The battery can further comprise means to impede transfer of chemically reactive species between the two half cells, which can be a non- conductive separator configured with open channels, grids or pores (claims 20 - 21) or a membrane (claim 26). Hence subject-matter of claims 5, 7-13 and 22 - 29 of present application is not novel with respect to D1.

2.2. Document D2 (US 4435257 A) describes an electrolytic process for the preparation of Fe(VI) salts in a membrane type electrolysis cell assembly, which comprises two half cells being in contact with and separated from each other through an ionomeric film (abstract). The process is carried out by supplying a direct current to the cell (column 6, line 18 - 20, and column 10, line 34), i.e. a **power supply is employed to perform the electrochemical reactions**. Hence, the abstract of D2 discloses the same combination of technical features as in claim 1, except for the condition that the amount of iron containing material is at least 1 weight %. However, in column 5, line 55 - 58, a range of ferric ion concentration of 0.001 - 12 %, preferably of 0.1 to 10 %, is disclosed. Since the "weight-%" of present application are not further specified, neither in the

claims nor in the description, it is assumed that they refer to the total mass of the anolyte. Hence, subject-matter of claim 1 is not novel.
In D2 it is further possible to use Fe(0), Fe(II) or Fe(III) compounds as the Fe source (column 5, line 45 - 50 and column 9, line 6 - 9). For example, D2 discloses the use of $Fe_2(SO_4)_3$ (example 2) or of $FeCl_3$ (column 7, line 10) as starting compounds and also mentions that iron oxide is formed on the anode (column 4, line 53). Further, D2 teaches that a sodium halide, such as chloride or bromide, or hypohalite, such as hypochlorite or hypobromite, should be present during oxidation (column 4, line 45 - column 5, line 57). The anolyte is an aqueous solution of these salts. The iron-containing anolyte is in direct contact with the electrically conducting anode, which can consist of different materials and can have different shapes (see column 4, line 1 - 34, and example 1). Further, there is a membrane between the cathode and the anode half-cell. Therefore subject-matter of claims 2 - 7, 12, 20 - 23, 25 - 29, is not novel.

2.3. Document D3 (US-A-5 217 584) is not novelty destroying, because it describes a process for the preparation of Fe(VI) salts by chemical oxidation of Fe_2O_3 employing hypohalites.

3. Inventive step (Article 33(3) PCT).

Subject-matter of claims 15 - 19, 31- 44 are not inventive for the reasoning as given below.

3.1. Objective problem with respect to the prior art.
Since the battery disclosed in D1 is reversible it can also be used for preparation of Fe(VI) salts. Hence, the technical problem as stated under 2.1., above, is already solved (otherwise the battery disclosed in D1 would not be reversible). Therefore, the technical problem consists in providing more specific process conditions and process details or to provide an improved process.

3.2. Subject-matter of claim 14 is considered as inventive, because the dissolution of a liquid in the neutral ionic conductor is not derivable nor hinted from D1 and D2 and a technical effect is shown in example 3, which uses a mixture of organic solvents.

3.3. Claim 15 is not inventive, since claim 31 of D1 already discloses hydroxide concentrations of up to saturation for aqueous solutions forming the electrically neutral ion conductor.

3.4. D1 describes on page 9, line 23, to page 10, line 5, that the electrolyte should contain a saturated concentration of a Fe(VI) salt in order to obtain a long half-time of the Fe(VI) salt. Also in D2 the concentration of the formed Fe(VI) salt can reach saturation (column 8, line 3 - 5). Finally it is obvious that, if the produced Fe(VI) salt is a solid, as it is the case in present application, it is also dissolved in the electrolyte with a saturated concentration. Hence, subject-matter of claims 16 and 17 is not inventive. Further, it is also obvious that in case of Fe(II) or Fe(III) salts as the starting material these salts will be dissolved in the electrolyte in concentrations of up to saturation. Therefore, claims 18 and 19 are not inventive.

3.5. Although the combination of technical features in claim 30 is not derivable from the prior art, no technical effect is shown, neither in the description of the preferred embodiments nor in the examples, for the feature that the "cathode includes a non metal inorganic salt capable of being reduced". Hence, this feature is considered as being not essential and subsequently subject-matter of claim 30 as not inventive.

3.6. D1 discloses some metals of being applicable as an anode (page 5, line 10 - 19). In D1, these metals are oxidised and thereby metal salts are formed. If the battery is reversed, said anode becomes the cathode and these metal salts are again reduced. Hence, subject-matter of claim 31 is obvious.
It is also possible to employ organic compounds, either aromatic or non-aromatic ones. For the sake of reversibility, however, a person skilled in the art will use such compounds which form stable organic product compounds upon their oxidation, which, in turn, can be reduced again. Therefore, subject-matter of claim 32 is obvious.

3.7. Claims 33 - 42 are not inventive, because D1 teaches that the Fe(VI) salt can contain different further cations (claim 2), such as Ba, Li, Sn, Mn, Co, In (page 3, line 20 - 28). If this Fe(VI) salt is reduced, these cations will be present as a salt beside the reduced Fe salt (with oxidation state e.g. +3). Hence, it is obvious to have another compound, which can be considered as an "additive" or an "added material" besides the Fe containing starting material. Although the limitation to 0.1 to 50% for the added

material results in a combination of technical features which is not derivable from D1 or D2, this limitation is unduly broad, since its meaning is not clear (see also item 6.4. under Clarity). D1 teaches further, that the ionic conductor can contain a solid solute or dissolved liquid (claim 22), which can be KOH, NaOH, or the like (claims 23 and 24). These materials are also considered to be "added materials" or "additives".
Regarding claim 41, although the use of a W additive is not derivable from D1 and D2, no technical effect is shown nor obvious. Moreover, the W additive is even not mentioned in one of the examples. Hence, a W additive is considered as mere guess but not as an essential feature.

3.8. Claims 43 and 44 are not inventive, since the use of oxides or hydroxides and transition metals is obvious from D1. If, as in example 4 of D1, Zn is used as the anode during discharging of the battery, it will be oxidised to from ZnO (equation 4), which under the given strong alkaline conditions also forms in part $Zn(OH)_2$ (and/or anions like $Zn(OH)_{3-}$). This oxide or hydroxide will form part of the cathode once the battery is charged and Fe(VI) salt is produced.

3.9. With respect to the comments above the technical problem to be resolved is to provide more process specifications on the from D1 and D2 known process of electrolytic formation of Fe(VI) salts. These specifications can be found in the examples of present application. However, subject-matter of the present claims is too broad and does not include new essential technical features, as for example given on pages 11 - 19, which would lead in combination with technical features from the prior art to new and subject-matter.

4. Industrial applicability (Article 33(4) PCT).
Claims 1 - 44 fulfill the requirement of industrial applicability, since subject-matter of present application can be made or used (in a technological sense) in industry (Article 33(4) PCT).

Re Item VII
Certain defects in the international application

5.1. Contrary to the requirements of Rule 5.1(a)(ii) PCT, the relevant background art

disclosed in the document D1 is not mentioned in the description, nor is this document identified therein. In addition, the statement which reads "but not specified the form of the recharged salts" is regarded as unnecessary and not in compliance with Rule 9.1.iv.

5.2. Subject-matter of claims 5, 6, 12 - 21, 43 - 44 is not supported by the description. According to Article 6 PCT, there must be a basis in the description for the subject-matter of every claim. The reasons are the following:
a) The compounds mentioned on page 4 and 5 refer to the final iron (VI) salt, whereas claims 5 and 6 refer to the Fe(II) or Fe(III) educt salts. Although the Applicant states that it is self-evident that the starting compounds must contain the same components that the final Fe(VI) salt, it could be possible that also the starting components undergo electrochemical changes. Support by the description means that the subject-matter of the claims can be derived from the description by somebody skilled in the art in an unambiguous and direct way.
b) Also the technical features of claims 12 - 21 cannot be found in the description.
c) In the description (page 6, line 26 - 29, and examples 2 and 3) the cathode materials are not disclosed in such a detail than in claims 43 and 44.

5.3. Table on page 12, bottom: it should read **tri**fluorosulfonate instead of **tetra**fluorosulfonate for TFMS.

5.4. Pages 14 and 16: "mAh" are a unit for a certain charge but not for an amount of material (e.g. 125 mAh of $BaOx1.5Fe_2O_3$)(Rule 10.1 PCT).

5.5. Pages 15 and 16: the unit "kg" is not a pressure unit. The pressure must be given in a unit of "force per area" not "mass per area", e.g. in "Pa", in order to comply with Rule 10.1 PCT.

5.6. Page 6, line 9 should read "anions" instead of "cations".

Re Item VIII

Certain observations on the international application

6. Clarity (Article 5 and 6 PCT).

6.1. Although claims 1, 29, 30, 41 and 44 have been drafted as separate independent claims, they appear to relate effectively to the same subject-matter and to differ from each other only with regard to a preferred embodiment. The aforementioned claims therefore lack conciseness. Moreover, lack of clarity of the claims as a whole arises, since the plurality of independent claims makes it difficult, if not impossible, to determine the matter for which protection is sought, and places an undue burden on others seeking to establish the extent of the protection. Hence, these claims do not meet the requirements of Article 6 PCT.

6.2. Claim 1: It is not fully clear by the wording alone where "at least 1 % of weight" refers to.

6.3. Claims 27 and 29: there is no reference in claims 1 - 4 for the expression "said anode", since none of these claims comprise the term "anode". Possibly, "cathode" is meant instead of "anode".

6.4. Claims 33, 34:
a) It is not clear what kind of "%" is meant, i.e. mol-%, weight-%, volume %. Hence, these claims are unduly broad and do not define the scope for which protection is sought.
b) Moreover, for claim 33 it is not clear by the wording alone what the term "added material" exactly comprises, because claims 12 and 16 - 21 already deal with a dissolved salt in the neutral ionic conductor, which is regarded as an added material.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
29 March 2001 (29.03.2001)

PCT

(10) International Publication Number
WO 01/21856 A1

(51) International Patent Classification[7]: C25B 1/28, H01M 4/58

(21) International Application Number: PCT/IL00/00588

(22) International Filing Date: 21 September 2000 (21.09.2000)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
132022 23 September 1999 (23.09.1999) IL

(71) Applicant *(for all designated States except US)*: CHEMERGY LTD. [IL/IL]; Gutwirth Science Based Industries Center, Technion City, 32000 Haifa (IL).

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(74) Agent: LAVIE, Simon; Elhanan St. 10, P.O.B 6202, 31061 Haifa (IL).

(81) Designated States *(national)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:
— *With international search report.*
— *Before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments.*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 01/21856 A1

(54) Title: ELECTROLYTIC PRODUCTION OF SOLID Fe(VI) SALTS

(57) Abstract: The invention relates to a novel preparation of Fe(VI) salts, also known as Super-iron or ferrates, based on direct electrolytic synthesis into the solid-phase. According to the invention there are two half-cells which are in an electro-chemical contact with one another through an electrically neutral ionic conductor, wherein one of said half-cells comprises a cathode and the other half cell comprises at least 1% by weight of an iron containing material, wherein a power supply is used to oxidize the iron containing material to a solid Fe(VI) salt.

ELECTROLYTIC PRODUCTION OF SOLID Fe(VI) SALTS

The present invention relates to the novel preparation of Fe(VI) salts. More particularly the invention relates to a method for the preparation of Fe(VI) salts, also known as Super-iron or ferrates, based on direct electrolytic synthesis into the solid-phase.

BACKGROUND OF THE INVENTION

There is an ongoing need for providing chemical oxidizing agents which are low-cost and are acceptable by the environment for a wide variety of applications including improved batteries, chemical synthesis and water purification. For example, for batteries, prima facie, salts containing iron in the +6 valence state, hereafter called Fe(VI) which are capable of multiple electron reduction, or multiple ion intercalation, would be capable to provide a higher cathode storage capacity.

Fe(VI) salts such as sodium, potassium and calcium/sodium ferrates, have been previously electrochemically formed by anodic dissolution which forms a solution containing dissolved Fe(VI). This has been reported by J. P. Deininger et al. (U.S. Patents 4451338, 4435257 and 435256), and more recently by Devir et al. (J. App. Electrochem. 26, 823-827, 1996) and by Bouzek et al (Electrochem. Commun. 1, 370-374, 1999). Following this, solid Fe(VI) salts may be recovered by precipitation as a solid adduct.

Electrochemical synthesis by anodic dissolution has several unattractive features. These include that Fe(VI) is produced only in a highly dilute, and hence less useful, form.

Typically Fe(VI) is synthesized by anodic dissolution only up to approximately 1% by weight, or less, of the solution. Another unattractive feature of anodic dissolution synthesis is the need for additional materials to recover by precipitation the solid Fe(VI) adduct. Still another unattractive feature of anodic dissolution synthesis is the loss of Fe(VI) during synthesis due to decomposition. This iron decomposition to a less oxidized form (i.e. to a lower valence state) can occur very rapidly. The stability of Fe(VI) salts solutions often being only on the order of a few hours at room temperature (Anal. Chem. 23, 1312-4, 1951). Later, in a report by H. Goff et al (J. Amer. Chem. Soc. 93, 6058-6065, 1971) it was mentioned that only little is known on the chemistry of Fe(VI) salts. The decomposition of iron to a lower valence, loses spontaneously the oxidative feature of the Fe(VI) salt. In its reaction with water the Fe(VI) as expressed in the form of the species FeO_4^{2-}, such as from the salt K_2FeO_4 is unstable in neutral aqueous solutions and decomposes according to the following equation:

$$2FeO_4^{2-} + 3H_2O \xrightarrow{k_f} 2FeOOH + 3/2O_2 + 4OH^- \qquad (1)$$

It is an object of the present invention to provide a novel method for electrochemical preparation of Fe(VI) salts which overcomes the unattractive features of anodic dissolution synthesis, and is therefore capable of producing concentrated Fe(VI), while also avoiding Fe(VI) decomposition losses during synthesis, and without the need for precipitating agents.

BRIEF DESCRIPTION OF THE INVENTION

The invention relates to an electrochemical process to prepare solid Fe(VI) salts, by an electrolytic cell comprising two half-cells which are in an electrochemical contact with one another through an electrically neutral ionic conductor, wherein one of said half-cells comprises a cathode and the other half-cell comprises at least 1% of weight of an iron containing material, wherein a power supply is used to oxidize the iron containing material to a solid Fe(VI) salt. Material additions to the iron containing material, and to the electrically neutral ionic conductor can change the characteristics of the prepared solid Fe(VI) salt.

BRIEF DESCRIPTION OF THE FIGURES

Figure 1: is a diagrammatic illustration of an electrolytic process for preparing solid Fe(VI) salts.

DETAILED DESCRIPTION OF THE INVENTION

The novel battery according to the present invention is based on Fe(VI) (hereafter also called "super iron") half cell in contact with a cathode half cell through an electrically neutral ionic conductor. The preparation of this solid super iron salt is based on the electrolytic oxidation of a half cell containing at least 1% by weight of iron in its 0 (metal or Fe(0)), and/or +2 (Fe(II)), and/or +3 (Fe(III) valence state. The electrically neutral ionic conductor has a Fe(VI) salt dissolving capacity less than the quantity of prepared Fe(VI) salt. This undissolved prepared Fe(VI) salt is in the solid phase. This overcomes the unattractive features of anodic dissolution synthesis, and is capable of producing more concentrated Fe(VI), which avoids solution phase Fe(VI) decomposition losses during synthesis, and which is formed without the need for precipitating agents.

The solid Fe(VI) salt is illustrated by $MFeO_4$, M being an alkali earth cation. Other typical examples includes a cation, selected from the alkali cations, in the form M_2FeO_4, or from the group consisting of the transition metal cations, or containing, cations of group III, group IV and group V elements, with charge +z, and of the form $M_{2/z}FeO_4$. Similarly Fe(VI) salts in addition to oxygen, can contain hydroxide and/or other anions, X, of charge -y, and of the generalized form: $M_{2/z}FeX_{8/y}$. The anion, X, include, but are not limited to: hydroxides, acetates, acetylsalicylates, alumminates, aluminum hydrides, amides, antomonides, arsenates, azides, benzoates, borates, bromides, bromates, carbides, carbonates, chlorates, perchlorates, chlorides, hypochlorites, chlorites, dithiones, chloroplatinates, chromates, citrates, fluorides,

fluosilicates, fluorosulfonates, formates, gallium hydrides, gallium nitrides, germanates, hydrides, iodates, iodides, periodate, laurates, manganates, malonates, permanganates, molybdates, myristates, nitrates, nitrides, nitrites, oxalates, oxides, palmitates, phosphates, salicylates, selenates, selenides, silicates, silicides, stearates, succinates, sulfates, sulfides, sulfites, tartrates, thiocyanates, thionates, tungstates, halides, or chalcogenides. Additionally, each Fe(VI) salts can contain n water or other solvent molecules, W of the generalized form, not limited to: $M_{2/z}FeX_{8/y} \cdot W_n$.

Examples thereof include, but are not limited to, K_2FeO_4, Na_2FeO_4, Li_2FeO_4, Cs_2FeO_4, Rb_2FeO_4, H_2FeO_4, $(NH_4)_2FeO_4$, $BeFeO_4$, $MgFeO_4$, $CaFeO_4$, $SrFeO_4$, $BaFeO_4$, $BaFeO_4 \cdot H_2O$, $BaFeO_4 \cdot 2H_2O$, Hg_2FeO_4, $HgFeO_4$, Cu_2FeO_4, $CuFeO_4$, $ZnFeO_4$, Ag_2FeO_4, $FeFeO_4$, $Fe_2(FeO_4)_3$, $MnFeO_4$, $NiFeO_4$, $CoFeO_4$, $Al_2(FeO_4)_3$, $In_2(FeO_4)_3$, $Ga_2(FeO_4)_3$, $SnFeO_4$, $PbFeO_4$, $Sn(FeO_4)_2$, $Pb(FeO_4)_2$.

Without being bound to any theory, the electrolytic oxidation of iron in its 0 (Fe(0)), +2 (Fe(II)) or +3 (Fe(III)) valence state, requires per iron a minimum electrolysis charge (current x time) sufficient to release 6, 4, or 3 electrons, respectively, in accord with:

$$Fe(0) \rightarrow Fe(VI) + 6e^- \qquad (2)$$

$$Fe(II) \rightarrow Fe(VI) + 4e^- \qquad (3)$$

$$Fe(III) \rightarrow Fe(VI) + 3e^- \qquad (4)$$

$$3Fe(8/3, \text{ as in } Fe_3O_4) \rightarrow 3\,Fe(VI) + 10e^- \qquad (5)$$

Generally the electrolysis charge time depends on the desired final FeO_4^{2-} concentration.

The Fe(0) in the half-cell is iron metal, in a typical embodiment of high surface area which includes iron powder, iron wire, iron screen or roughened iron surfaces or in another typical embodiment sheet or solid iron. The iron salt used in the synthesis in the half-cell is in the solid or dissolved state. Fe(II) salts includes, but are not limited to FeO, $Fe(OH)_2$, and salts of the general form $M_zFe(II)X_y \cdot W_n$. which contains z or one or more cations, M, and y of one or more cations X, and n of on or more solvent molecules W. The Fe(III) salt includes, but is not limited to Fe_2O_3, FeOOH, $Fe(OH)_3$, and salts of the general form $M_zFe(III)X_y \cdot W_n$. which contains z or one or more cations, M, and y of one or more cations X, and n of on or more solvent molecules W. Alternately, a salt of intermediate valence, such as Fe_3O_4, can be used as the iron salt.

The iron (Fe(0), Fe(II) or Fe(III)) which is to be oxidized is placed in contact with a conductive material, such as graphite, carbon black or a metal. These and other agents can be formed by mixing with the iron as a powder, and the powder can be pressed with these and other agents to improve mechanical strength. Rather than mixing with a conductive material, the iron salt can be placed in direct contact with a conductive material. These conductive materials include, but are not limited to a planar conductive surface, a wire, a porous conductive substrate or a conductive grid.

The cathode of the battery may be selected from the known list of materials capable of being reduced, typical examples being metal and non-metal inorganic salts, and organic compounds including aromatic and non-aromatic compounds.

The electrically neutral ionic conductor utilized in the battery according to the present invention, comprises a medium that can support current density during battery discharge. Typical representative ionic conductor is an aqueous solutions preferably containing a high concentration of a hydroxide such as KOH.

In typical embodiments, the electrically neutral ionic conductor comprises common ionic conductor materials used in electrolytic processes which include, but are not limited to an aqueous solution, a non-aqueous solution, a conductive polymer, a solid ionic conductor and a molten salt.

According to another embodiment, the invention provides means to impede transfer of chemically reactive species, or prevent electric contact between the anode and Fe(VI) salt cathode. Said means includes, but is not limited to a membrane a ceramic frit, or agar solution, positioned to separate said half cells or a non-conductive separator configured with open channels, grids or pores.

A material addition, from 0.1 to 50%, and in the preferred range from 1 to 10%, to the electrically neutral ionic conductor, or to the iron in its 0, +2 or +3 valence state, can modify the quantity and the physical, chemical and electrochemical characteristics of the Fe(VI) salt which will be formed, and or modify the voltage and coulombic efficiency of the Fe(VI) electrolytic formation process. A material addition of a barium compound, can be used to decrease the solubility of Fe(VI) salts to improve the quantity of Fe(VI) salt produced. Barium additions include, but are not limited to, barium(II) compounds, as illustrated by BaX_2 and BaY_3, where X and Y are anions as previously described.

A material addition of an oxygen containing compound, be used to increase quantity of Fe(VI) salt produced. Oxygen containing compounds include, but are not limited to, hydroxide compounds, such as MOH compounds, M being an alkali cation. Another typical example of hydroxides salts contain alkali earth, M' cations, other typical examples includes a cation, selected from the group consisting of the transition metal cations, or containing, cations of group III, group IV and group V elements. Another typical example of oxygen containing compounds includes oxides containing alkali, alkali earth, M' cations, or a cation, selected from the group consisting of the transition metal cations, or containing, cations of group III, group IV and group V elements.

A material addition of a manganese compound, can be used. Manganese additions include, but are not limited to, manganese(IV) compounds, as illustrated by MnO_2, $Mn(OH)_4$, MnO_2, or MnS_2, manganese(III) salts, as illustrated by Mn_2O_3, and $Mn(OH)_3$, and Mn(II) salts, as illustrated by MnO, and $Mn(OH)_2$. Other typical manganese additions are manganese(VII) compounds illustrated by a permanganate salt $MMnO_4$, or Mn_2O_7, or manganese(VI) compounds illustrated by manganate salt, M_2MnO_2, M being an alkali cation. Another typical example of manganate and permanganate salts contain alkali earth, M' cations, other typical examples includes a cation, selected from the group consisting of the transition metal cations, or containing, cations of group III, group IV and group V elements.

A material addition of a cobalt compound can be used. Cobalt additions include, but are not limited to, cobalt(III) compounds, as illustrated by Co_2Y_3, or CoX_3, Y being oxygen or

in other typical examples being a chalcogenide, chromate, molybdate, silicate, malonate, succinate, tartrate, selenate, sulfate, or sulfite anions. X being a hydroxide anion, or in other typical examples, X being a halide anion, nitrate, bromate, chlorate, perchlorate, acetate, oxalate, carbonate, benzoate, hypochlorite, chlorite, dithionate, formate, iodate, or periodate anions. Other typical cobalt additions are Co(II) compounds such as CoY, CoX_2 and Co(IV) compounds such as and CoY_2, and CoX .

A material addition of lithium containing compound, can be used. Lithium containing compounds include, but are not limited to lithium: hydroxides, carbonates, acetates, acetylsalicylates, alumminates, aluminum hudrides, amides, antomonides, arsenates, azides, benzoates, borates, bromides, carbides, chlorates, perchlorates, chlorides, chloroplatinates, chromates, citrates, fluorides, fluosilicates, fluosulfonates, formates, gallium hydrides, gallium nitrides, germanates, hydrides, iodates, iodides, laurates, manganates, permanganates, molybdates, myristates, nitrates, nitrides, nitrites, oxalates, oxides, palmitates, phosphates, salicylates, selenides, silicates, silicides, stearates, sulfates, sulfides, sulfites, tartrates, thiocyanates, thionates, tungstates, or a material capable of incorporating the lithium ions, including but not limited to a carbon based material, or a tin based material, or a lithium intercalating material.

A material addition of various salts can be used to alter the required electrolysis voltage and/or alter the characteristics of the produced Fe(VI) salt. These compounds include indium compounds, which can lower the required

electrolysis voltage, tin compounds, such as SnO, and SnO_2, tungsten compounds, such as WO_3, and WO_2, and cobalt compounds, such as CoO and Co_2O_3. Indium additions include, but are not limited to, indium(III) compounds, as illustrated by In_2Y_3, or InX_3, where X and Y are previously described. Other typical indium additions are In(II) compounds as InY, InX_2 and In(IV) compounds such as and InY_2, and InX_4.

DETAILED DESCRIPTION OF FIGURE 1

Figure 1 illustrates schematically an electrochemical cell (10) based on an Fe(0), Fe(II) or Fe(III) half cell, an electrically neutral ionic conductor and an cathode. The cell contains an electrically neutral ionic conductor (22), such as a concentrated aqueous solution of KOH or $Ba(OH)_2$, or a non-aqueous solution containing a lithium salt, in contact with an Fe(0), Fe(II) or Fe(III) anode (14), typically a Fe(III) salt as a pressed pellet containing conductive powder, typcially carbon black, and generating an Fe(VI) salt such as $BaFeO_4$, K_2FeO_4, or Li_2FeO_4 during the synthesis. Oxidation of Fe(0), Fe salts is achieved via electrons removed by the power supply (14) to form the solid Fe(VI) salt. The cathode electrode 12, receives this electrons, such as in the form of a metal salt, is also in contact with the electrically neutral ionic conductor (22). Electrons are released in the oxidation of the anode. Optionally, the cell may contain an ion selective membrane or non-selective membrane (20) as a separator, for minimizing the non-electrochemical interaction between the cathode and the anode.

The invention will be hereafter illustrated by the following Examples, being understood that the Examples are

presented only for a better understanding of the invention without implying any limitation thereto, the invention being covered by the appended Claims.

EXAMPLE 1

An experiment was carried out, the object being to determine electrically neutral ionic conductors which have a limited Fe(VI) salt dissolving capacity, and which are thereby in a cell are compatible to produce solid Fe(VI) salt. For a cell containing a volume, V, of solution, the maximum dissolving capacity is V x S. S is the maximum solubility of the Fe(VI) salt in various electrically neutral ionic conductors. A lower value of S will increase the fraction of produced Fe(VI) which is in the solid state. A very low value of S will determine that the significant majority of produced Fe(VI) salt is in the solid state. A variety of solutions can be used as electrically ionic conductors. Table 1 presents the measured solubility of two examples of Fe(VI) salts, $BaFeO_4$ and K_2FeO_4, in a variety of solutions. As seen in Table 1, each of these solutions has a limited solubility of Fe(VI) salt and can be used to produce solid Fe(VI) salt when it is formed in a quantity greater than the limited dissolving capacity.

Table 1. Examples of the dissolving capacity of various aqueous and non-aqueous solutions for Fe(VI) salts, as expressed by the solution solubility; where for a cell containing a volume, V, of solution, the dissolving capacity is V x the Solubility. $LiClO_4$, LiTFB, LiTFMS refers to 1M, molar. in lithium perchlorate, or 1M in lithium tetrafluoroborate, or 1M lithium tetrafluoromethane sulfonate.

Solution	Salt	S, Solubility
water	$BaFeO_4$	<< 10^{-5} **M**
aqueous 0.2 M $Ba(OH)_2$	$BaFeO_4$	<< 10^{-5} **M**
aq. 5 M KOH & satd $Ba(OH)_2$	$BaFeO_4$	< $2x10^{-4}$ **M**
aq. 5 M KOH & satd $Ba(OH)_2$	K_2FeO_4	< $2x10^{-4}$ **M**
aq. 5 M KOH	$BaFeO_4$	$5x10^{-4}$ **M**
aq. 5 M KOH	K_2FeO_4 + $Ba(OH)_2$	$5x10^{-4}$ **M**
aq. 5 M KOH	K_2FeO_4	$7x10^{-2}$ **M**
aq. 5 M LiOH	K_2FeO_4	$9x10^{-1}$ **M**
aq. 5 M NaOH	K_2FeO_4	1.4 **M**
aq. 5 M CsOH	K_2FeO_4	$3.5x10^{-2}$ **M**
aq. 10 M NaOH	K_2FeO_4	$5x10^{-1}$ **M**
aq. 10 M KOH	K_2FeO_4	$1x10^{-2}$ **M**
aq. satd. KOH	K_2FeO_4	$2x10^{-3}$ **M**
acetonitrile (ACN)	$BaFeO_4$, K_2FeO_4	<< 10^{-5} **M**
ACN $LiClO_4$, LiTFB, LiTFMS	$BaFeO_4$, K_2FeO_4	<< 10^{-5} **M**
Propylene carbonate (PC)	$BaFeO_4$, K_2FeO_4	<< 10^{-5} **M**
PC $LiClO_4$, LiTFB, LiTFMS	$BaFeO_4$, K_2FeO_4	<< 10^{-5} **M**
acetone	$BaFeO_4$, K_2FeO_4	<< 10^{-5} **M**
hexane	$BaFeO_4$, K_2FeO_4	<< 10^{-5} **M**
chloroform	$BaFeO_4$, K_2FeO_4	<< 10^{-5} **M**
sulfonane	$BaFeO_4$, K_2FeO_4	<< 10^{-5} **M**
1,4 - dioxane	$BaFeO_4$, K_2FeO_4	<< 10^{-5} **M**
ethylene carbonate (EC)	$BaFeO_4$, K_2FeO_4	<< 10^{-5} **M**
EC + 0.5 **M** $LiClO_4$	$BaFeO_4$, K_2FeO_4	<< 10^{-5} **M**
γ-butyrlactone (BLA)	$BaFeO_4$, K_2FeO_4	<< 10^{-5} **M**
BLA + 0.5 **M** $LiClO_4$	$BaFeO_4$, K_2FeO_4	<< 10^{-5} **M**
tetrahyrofuran (THF)	$BaFeO_4$, K_2FeO_4	<< 10^{-5} **M**
THF + 1 **M** $LiClO_4$	$BaFeO_4$, K_2FeO_4	<< 10^{-5} **M**
Dimethoxyethane (DME)	$BaFeO_4$, K_2FeO_4	<< 10^{-5} **M**
DME $LiClO_4$, LiTFB, LiTFMS	$BaFeO_4$, K_2FeO_4	<< 10^{-5} **M**
Dimethylformamide (DMF)	$BaFeO_4$, K_2FeO_4	<< 10^{-5} **M**
DMF + 1 **M** LiTFMS	$BaFeO_4$, K_2FeO_4	<< 10^{-5} **M**
Dimethylsulfoxide (DMSO)	$BaFeO_4$, K_2FeO_4	<< 10^{-5} **M**
DMSO + 1 **M** $LiClO_4$	$BaFeO_4$, K_2FeO_4	<< 10^{-5} **M**

Example 2

An experiment was carried out, the object being to produce electrolytic solid Fe(VI) salt using an electrochemical cell as diagrammatically illustrated in Fig. 1. The electrochemical cell configuration consisted of a 2 cm diameter button cell comprised of an upper (cathode) section, pressing onto a mid (separator) section, pressing onto a lower (anode) section.

The upper section of the electrochemical cell configuration comprises an upper inverted metal dish plate (the cathode cap) pressing onto a metal washer type spring, which presses onto a metal screen (the cathode collector), pressing onto a metal hydride material removed from a discharge commercial metal hydride battery. The quantity of metal hydride is determined to be in coulombic excess of the iron starting material, as determined in accord with equations 2-5. The mid section consists of a separator material removed from a commercial metal hydride battery and is surrounded by a PTFE washer to prevent direct contact or electrical shorting of the upper and lower section. Various electrolytes as electrically neutral ionic conductors, in various amounts, were tested, and are added to the separator and anode material. The lower section consists of a pressed mixed powder pressed into a bottom metal dish plate. Various cells were formed with powders containing a variety of iron materials in the Fe(0), Fe(II), or Fe(III) valence state, as well as various tested additives and added conductors.

An oxidizing current was applied to the anode using a constant current power supply connected for a fixed time to the upper and lower plates of the electrochemical cell

configuration. A variety of currents and times were examined in various cells. Each cell was then opened, and the solid iron material was removed. The percentage of the original iron containing material that was converted to solid Fe(VI) salt was determined by the chromite method to probe the iron valence state, determined by Fe(VI) redissolution as FeO_4^{2-}, and oxidation of chromite, according to (where chromate generated is titrated with a standard ferrous ammonium sulfate solution, using a sodium diphenylamine sulfonate indicator):

$$Cr(OH)_4^- + FeO_4^{2-} + 3H_2O \rightarrow Fe(OH)_3(H_2O)_3 + CrO_4^{2-} + OH^- \quad (6)$$

Tables 2-4 summarizes the percentage of Fe(VI) salt that was produced from the original iron containing material for a variety of formed electrolytic cells. As can be seen in the tables, various solid Fe(VI) salts can be directly formed by this procedure, and this procedure varies with added conductor, additives, electrolyte and electrolysis time and current. In each case of the experiments summarized in Tables 2-4, 25 mAh of an iron material. as determined by equation 2, 3, 4 or 5. is used as the synthesis starting material In the tables for the anode mix, the molar ratio of any additive is indicated, as well the percent by weight of the conductor. Also in the Table, $Ba(OH)_2$ represents $Ba(OH)_2 \cdot 8H_2O$, 13.5KB represents 13.5 M KOH with saturated $Ba(OH)_2$, CB represents carbon black, and grf represents graphite. In Table 2, materials examined as synthesis starting material include Fe powder. The Fe(II) salts, FeO and FeC_2O_4. Fe_3O_4, and the Fe(III) salts Fe_2O_3, $Fe(NO_3)_3$, $FeCl_3$.

In Table 3 materials incorporating both cations and iron have been used as the starting material. These include I = $K_2O \cdot 1.5Fe_2O_3$, II = $Li_2O \cdot 1.5Fe_2O_3$, III = $CaO \cdot 1.5Fe_2O_3$, IV =

$BaO \cdot 1.5Fe_2O_3$, and V $2BaO \cdot Fe_2O_3$. The latter are produced from stoichiometric mixtures of a carbonate or $Ba(OH)_2 \cdot 8H_2O$, and Fe_2O_3 (< 5μm, 99+%, Aldrich Chemical), pressing the mixture at 1000 kg, and heating in air at 900℃ for 24 hours produced according to:

$$2K_2CO_3 + 3Fe_2O_3 \rightarrow K_2O \cdot 1.5Fe_2O_3 + 2CO_2(gas) \quad (7)$$

$$2Li_2CO_3 + 3Fe_2O_3 \rightarrow Li_2O \cdot 1.5Fe_2O_3 + 2CO_2(gas) \quad (8)$$

$$2CaCO_3 + 3Fe_2O_3 \rightarrow CaO \cdot 1.5Fe_2O_3 + 2CO_2(gas) \quad (9)$$

$$2BaCO_3 + 3Fe_2O_3 \rightarrow BaO \cdot 1.5Fe_2O_3 + 2CO_2(gas) \quad (10)$$

$$2Ba(OH)_2 \cdot 8H_2O + Fe_2O_3 \rightarrow 2BaO \cdot Fe_2O_3 + 10H_2O(gas) \quad (11)$$

The experiments summarized in Tables 2-4 are provided only by way of example, and are not limiting. It is evident that further variation of the many cell parameters including, but not limited to particle size of the pressed anode powders, anode and electrolyte composition, the separator and cathode type and thicknesses, and other electrolysis conditions can be used to further increase the efficiency, percentage and type of the produced(VI) solid salt. This is exemplified in Table 4, in which synthesis parameters are varied for one starting material, $BaO \cdot 1.5Fe_2O_3$. The $BaO \cdot 1.5Fe_2O_3$ is used as produced, or sorted by particle size through various mesh size sieves (for example, a 390 mesh screen is used to sort the < 35μm particles).

As a continued example, the following experiment was conducted to demonstrate that the electrosynthesis may be scaled up, and that the super-iron purity may be further enhanced. A cell of 4 cm diameter, with 4 times the surface area of the pervious 2 cm diameter electrosynthesis cell, was employed. A 4 cm^2 cadmium electrode, to be used as the synthesis cathode, and 4 cm^2 separators, both cut upon

removal from an opened AA cylindrical Ni-Cd battery, were used. In one case, the starting material was 125 mAh of $BaO\cdot 1.5Fe_2O_3$, prepared in accord with equation 10. In addition, the starting anode mix contains a 1:2 molar ratio of $Ba(OH)_2\cdot 8H_2O$ to $BaO\cdot 1.5Fe_2O_3$, and 25% by weight of carbon black. The anode mix was pressed at 1000 kg into the anode compartment. Then, 0.37 grams of 13.5 M KOH electrolyte was soaked on the anode mix for 12 hours, and subsequently the separator and cathode were pressed into the cell. A 10 mA current was applied to the anode, through the cell for 50 hours. The anode material was removed, and the product contained 82.9% conversion of Fe(III) into solid Fe(VI), such as $BaFeO_4$, as determined by chromite analysis.

In a second case in the 4 cm diameter synthesis cell, the anode mix contained 50 mAh of $2BaO\cdot Fe_2O_3$. The $2BaO\cdot Fe_2O_3$ was prepared from $2BaCO_3$ and Fe_2O_3, pressing the mixture at 1000 kg, and heating in air at 900°C for 24 hours. The anode mix also contained 25% by weight KOH, 25% carbon black, as well as 1% $Ba(OH)_2\cdot 8H_2O$ and 2% KIO_4. The anode mix was pressed at 1000 kg into the anode compartment. Then, 0.32 grams of 13.5 M KOH electrolyte was soaked on the anode mix for 12 hours, and subsequently the separator and cathode were pressed into the cell. A 50 mA current was applied to the anode, through the cell for 3 hours. The anode material was removed, and the product contained 75.2% conversion of Fe(III) into solid Fe(VI), as determined by chromite analysis.

Table 2. Electrochemical synthesis of Fe(III) using various starting materials under different conditions.

Starting Fe material in anode	anode additive ratio or wt%	Conductor wt% anode	mass electrolyte added per g anode	Charging current, time	% Fe(VI) produced
Fe(0)	BaO/(1:1)	40% CB	0.5g 13.5 KB	2 mA, 30 hr	9.2%
Fe	$Ba(OH)_2$/(1:1)	40% CB	0.5g 13.5 KB	2 mA, 30 hr	21.1%
Fe(II)O	$Ba(OH)_2$/(1:3)	40% CB	0.5g 13.5 KB	2 mA, 30 hr	25.7%
$Fe(II)C_2O_4 \cdot 2H_2O$	$Ba(OH)_2$/(1:1)	30% CB	1.5g 13.5 KB	2 mA, 60 hr	58.9%
$Fe(II)C_2O_4 \cdot 2H_2O$	$Ba(OH)_2$/(1:1)	30% CB	1.5g 13.5 KB	2 mA, 60 hr	38.4%
Fe_3O_4	$Ba(OH)_2$/(1:3)	40% CB	0.5g 13.5 KB	2 mA, 30 hr	31.8%
Fe_3O_4	$Ba(OH)_2$/(1:3)	30% CB	0.5g 13.5 KB	2 mA, 30 hr	39.1%
Fe_3O_4	$Ba(OH)_2$/(1:3)	30% CB	0.75g 13.5 KB	2 mA, 40 hr	42.7%
Fe_3O_4	BaO/(1:1.5)	30% CB	0.75g 13.5 KB	2 mA, 40 hr	19.0%
$Fe(III)_2O_3$	$Ba(OH)_2$/(1:3)	30% CB	0.5g 13.5 KB	2 mA, 30 hr	34.7%
Fe_2O_3	$Ba(OH)_2$/(1:1)	30% CB	0.75g 13.5 KB	2 mA, 40 hr	41.1%
Fe_2O_3	$Ba(OH)_2$/(1:2)	30% CB	0.75g 13.5 KB	2 mA, 40 hr	26.3%
$Fe(III)(NO_3)_3 \cdot 9H_2O$	$Ba(OH)_2$/(1:1)	20% CB	0.25g 13.5 KB	2 mA, 40 hr	32.3%
$Fe(III)Cl_3 \cdot 6H_2O$	$Ba(OH)_2$/(1:1)	20% CB	0.25g 13.5 KB	2 mA, 40 hr	34.2%

Table 3. Electrochemical synthesis of Fe(III) using various starting materials incorporating both cations and iron under different conditions.

Starting Fe material in anode	anode additive ratio or wt%	Conductor wt% anode	mass electrolyte added per g anode	Charging current, time	% Fe(VI) produced
$I=K_2O \cdot 1.5Fe_2O_3$	KOH/(1:1)	30% CB	0.5g 12M KOH	3 mA, 20 hr	2.2%
$II=Li_2O \cdot 1.5Fe_2O_3$	LiOH(1:1)	30% CB	saturated LiOH	3 mA, 20 hr	2.2%
$III=CaO \cdot 1.5Fe_2O_3$	$Ca(OH)_2$(1:2)	30% CB	saturated $Ca(OCl)_2$	3 mA, 20 hr	2.6%
$IV=BaO \cdot 1.5Fe_2O_3$	$Ba(OH)_2$/(1:2)	30% CB	0.5g 13.5 KB	2 mA, 40 hr	57.3%
$V=2BaO \cdot Fe_2O_3$	no $Ba(OH)_2$	30% CB	0.5g 13.5 KB	2 mA, 40 hr	62.5%
V	10% $Ba(OH)_2$	30% CB	0.5g 13.5 KB	2 mA, 40 hr	54.3%
V	15% $Ba(OH)_2$	30% CB	0.5g 13.5 KB	2 mA, 40 hr	49.8%
V	20% $Ba(OH)_2$	30% CB	0.5g 13.5 KB	2 mA, 40 hr	44.5%

Table 4. Electrochemical synthesis of Fe(III) using $BaO \cdot 1.5Fe_2O_3$ under different conditions.

Starting Fe material in anode	anode additive ratio or wt%	Conductor wt% anode	mass electrolyte added per g anode	Charging current, time	% Fe(VI) produced
IV=$BaO \cdot 1.5Fe_2O_3$	$Ba(OH)_2$/(1:2)	40% CB	0.5g 13.5 KB	2 mA, 30 hr	69.1%
IV	$Ba(OH)_2$/(1:2)	40% CB	0.5g 13.5 KB	2 mA, 50 hr	67.7%
IV <35μm particles	$Ba(OH)_2$/(1:2)	30% CB	0.5g 13.5 KB	2 mA, 40 hr	64.5%
IV 35-53μm particles	$Ba(OH)_2$/(1:2)	30% CB	0.5g 13.5 KB	2 mA, 40 hr	62.0%
IV 53-73μm particles	$Ba(OH)_2$/(1:2)	30% CB	0.5g 13.5 KB	2 mA, 40 hr	57.1%
IV >73μm particles	$Ba(OH)_2$/(1:2)	30% CB	0.5g 13.5 KB	2 mA, 40 hr	54.7%
IV	BaO(1:2)&10%CsOH	40% CB	0.5g 13.5 KB	2 mA, 30 hr	65.6%
IV	BaO(1:2)	40% CB	1g 13.5 K	2 mA, 30 hr	58.2%
IV	BaO(1:2)	40% CB	0.75g 13.5 KB	2 mA, 30 hr	61.6%
IV	BaO(1:2)	40% CB	0.5g 13.5 KB	2 mA, 30 hr	66.2%
IV	BaO(1:2)	40% CB	0.25g 13.5 KB	2 mA, 30 hr	41.5%
IV	BaO(1:2)&10%KOH	40% CB	0.5g 13.5M KOH	2 mA, 30 hr	59.3%
IV	BaO(1:2)	40% CB	0.5g 13.5M KOH	2 mA, 30 hr	61.9%
IV	BaO(1:2)	30% CB	0.5g 13.5M KOH	2 mA, 30 hr	52.8%
IV	BaO(1:2)	10% CB	0.5g 12M KOH	2 mA, 30 hr	16.0%
IV	BaO(1:2)	20% CB	0.5g 12M KOH	2 mA, 30 hr	35.3%
IV	BaO(1:2)	30% CB	0.5g 12M KOH	2 mA, 30 hr	48.3%
IV	BaO(1:2)	40% CB	0.5g 12M KOH	2 mA, 30 hr	56.8%
IV	BaO(1:2)	50% CB	0.5g 12M KOH	2 mA, 30 hr	54.2%
IV	BaO(1:2)	60% CB	0.5g 12M KOH	2 mA, 30 hr	50.7%
IV	BaO(1:2)	30% CB	0.5g 10M KOH	2 mA, 30 hr	25.9%
IV	BaO(1:2)	30% CB	0.5g 8M KOH	2 mA, 30 hr	12.3%
IV	BaO(1:2)	30% CB	0.5g 6M KOH	2 mA, 30 hr	10.6%
IV	BaO(1:2)	30% CB	0.5g 12M KOH	2 mA, 60 hr	49.3%
IV	BaO(1:2)	30% CB	0.5g 12M KOH	2 mA, 20 hr	44.6%
IV	BaO(1:2)	30% CB	0.5g 12M KOH	2 mA, 10 hr	31.0%
IV	BaO(1:2)	30% CB	0.5g 12M KOH	2 mA, 5 hr	25.2%
IV	BaO(1:2)	30% CB	0.5g 12M KOH	3 mA, 20 hr	49.1%
IV	BaO(1:2)	30% CB	0.5g 12M KOH	1 mA, 60 hr	31.9%
IV	BaO(1:2)	30% CB	0.5g 12M KOH	0.5 mA, 120hr	26.9%
IV	BaO(1:2)	30% CB	0.5g 12M KOH	10 mA, 6 hr	43.0%
IV	$Ba(OH)_2$(1:1)	30% grf	0.5g 12M KOH	3 mA, 20 hr	12.7%
IV	no $Ba(OH)_2$	30% grf	saturated $Ba(OH)_2$	3 mA, 20 hr	8.4%

Example 3

An experiment was carried out, the object being to produce using a non aqueous electrolyte, solid Fe(VI) salt using an electrochemical cell as diagramtically illustrated in Fig. 1. The cell configuration consisted of a 2.3 cm diameter button cell comprised of an upper (cathode) section, pressing onto a mid (separator) section, pressing onto a lower (anode) section. The upper section of the electrochemical cell configuration comprises an upper inverted metal dish plate (the cathode case) pressing onto a Li-ion electrode, removed from a discharged commercial Li-ion battery, and determined in accord with equation 4, to be in coulombic excess of the iron starting material. The mid section consists of separator materials removed from commercial Li-ion batteries, and is surrounded by a washer to prevent direct contact or electrical shorting of the upper and lower section. An electrolyte was added to the separator and anode mix. The electrolyte was comprised of 350mg of 1M $LiPF_6$ in a 1:1 ratio EC to DEC (ethylene carbonate to dimethylethylene carbonate). The lower section consists of a mixed material (53.9mg Fe_2O_3, 32.4mg LiOH, 86.5mg $LiClO_4$, and 57.3mg carbon black) pressed into a bottom metal dish plate, the anode case. An oxidizing current of 1 mA was applied to the anode using a constant current power supply connected through the cell for 28 hours. The cell was then open, and the solid iron material was removed. The percentage of the original iron containing material that was converted to solid Fe(VI) salt was determined by the chromite method, equation 6, and was analyzed at 65.3% conversion of Fe(III) to Fe(VI), such as Li_2FeO_4.

CLAIMS:

1. A process for preparing Fe(VI) salts which comprising two half-cells which are in an electrochemical contact with one another through an electrically neutral ionic conductor, wherein one of said half-cells comprises a cathode and the other half-cell comprises at least 1% of weight of an iron containing material, wherein a power supply is used to oxidize the iron containing material to a solid Fe(VI) salt.

2. The process according to Claim 1, wherein said iron containing material is a solid or dissolved Fe(III) salt.

3. The process according to Claim 1, wherein said iron containing material is a solid or dissolved Fe(II) salt.

4. The process according to Claim 1, wherein said iron containing material is iron metal, Fe(0).

5. The process according to Claim 2 or 3, wherein said salt is an oxide or a hydroxide or contains the anions, selected from the group consisting of acetates, acetylsalicylates, alumminates, aluminum hudrides, amides, antomonides, arsenates, azides, benzoates, borates, bromides, bromates, carbides, carbonates, chlorates, perchlorates, chlorides, hypochlorites, chlorites, dithionate, chloroplatinates, chromates, citrates, fluorides, fluosilicates, fluosulfonates, formates, gallium hydrides, gallium nitrides, germanates, hydrides, iodates, iodides, periodate, laurates, manganates, malonates, permanganates, molybdates, myristates, nitrates, nitrides, nitrites, oxalates, palmitates, phosphates, salicylates, selenates, selenides, silicates, silicides, stearates, succinates, sulfates, sulfides, sulfites, tartrates, thiocyanates, thionates, tungstates, halides, or chalcogenides.

6. The process according to Claim 2 or 3, wherein said salt includes a cation, selected from the group consisting of the alkali cations, H^+, the alkali earth cations, transition metal cations, or containing cations of group III, group IV and group V or ammonium or organic ammonium cations.

7. The process according to Claims 1 to 4, wherein said electrically neutral ionic conductor is an aqueous solution.

8. The process according to Claims 1 to 4, wherein said electrically neutral ionic conductor is a nonaqueous solution.

9. The process according to Claims 1 to 4, wherein said electrically neutral ionic conductor is a conductive polymer.

10. The process according to Claims 1 or 2, wherein said electrically neutral ionic conductor is a solid ionic conductor.

11. The process according to Claims 1 to 4, wherein said electrically neutral ionic conductor is a molten salt.

12. The process according to Claims 7 to 11, wherein said neutral ionic conductor contains a dissolved salt.

13. The process according to Claims 7 to 9, wherein said neutral ionic conductor contains a dissolved liquid.

14. The process according to Claim 13, wherein said dissolved liquid is an organic solvent.

15. The process according to Claims 7-11, wherein said neutral ionic conductor contains the concentration of up to saturation in hydroxide ions.

16. The process according to Claim 12, wherein said dissolved salt is an iron salt in a concentration of up to saturation.

17. The process according to Claim 16, wherein said iron salt an Fe(VI) salt.

18. The process according to Claim 16, wherein said iron salt an Fe(III) salt.

19. The process according to Claim 16, wherein said iron salt an Fe(II) salt.

20. The process according to Claim 12, wherein said dissolved salt is an oxide or a hydroxide or contains the anions, selected from the group consisting of acetates, acetylsalicylates, alumminates, aluminum hudrides, amides, antomonides, arsenates, azides, benzoates, borates, bromides, bromates, carbides, carbonates, chlorates, perchlorates, chlorides, hypochlorites, chlorites, dithionate, chloroplatinates, chromates, citrates, fluorides, fluosilicates, fluosulfonates, formates, gallium hydrides, gallium nitrides, germanates, hydrides, iodates, iodides, periodate, laurates, manganates, malonates, permanganates, molybdates, myristates, nitrates, nitrides, nitrites, oxalates, palmitates, phosphates, salicylates, selenates, selenides, silicates, silicides, stearates, succinates, sulfates, sulfides, sulfites, tartrates, thiocyanates, thionates, tungstates, halides, or chalcogenides.

21. The process according to Claim 12, wherein said dissolved salt includes a cation, selected from the group consisting of the alkali cations, H^+, the alkali earth cations, transition metal cations, or containing cations of group III, group IV and group V or ammonium or organic ammonium cations.

22. The process according to Claims 1 to 4, further characterized in that said iron containing material is in contact with a conductive material.

23. The process according to Claim 22, wherein said conductive material is selected from graphite, carbon black and a metal.

24. The process according to Claim 22, wherein said iron containing material-conductive material comprises a mixed pressed powder.

25. The process according to Claim 22, wherein said iron containing material-conductive material comprises a planar surface or a wire.

26. The process according to Claim 22, wherein said iron containing material-conductive material comprises a porous substrate or grid.

27. The process according to Claims 1 to 4 further comprising means to impede transfer of chemically reactive species between said anode and said other half cell.

28. The process according to Claim 27, wherein said means is a non conductive separator configured with open channels, grids or pores.

29. The process according to Claim 26 in which said means to impede transfer of chemically reactive species comprises a membrane positioned to separate said half cells.

30. The process according to Claim 1, wherein said cathode includes a non metal inorganic salt capable of being reduced.

31. The process according to Claim 1, wherein said cathode includes a metal inorganic salt capable of being reduced.

32. The process according to Claim 1, wherein said cathode includes an organic compound capable of being reduced.

33. The process according to Claim 32, wherein said organic compound is selected from the group consisting of aromatic and non-aromatic compounds.

34. The process according to Claims 1, further characterized in that said neutral ionic conductor contains an added enhancing material to modify the Fe(VI) salt production.

35. The process according to Claims 1 to 4, further characterized in that said iron containing material contains an added enhancing material to modify the Fe(VI) salt production.

36. The process according to Claim 34 or 35, wherein said enhancing material is a Ba(II) compounds.

37. The process according to Claim 34 or 35, wherein said enhancing material is an oxygen containing compound, such as an oxide or hydroxide compound.

38. The process according to Claim 34 or 35, wherein said enhancing material is an indium containing compound.

39. The battery according to Claim 1, wherein said enhancing material is a manganese containing compound.

40. The process according to Claim 10, wherein said charging voltage altering material, is a lithium containing compound.

41. The process according to Claim 34 or 35, wherein said enhancing material is a tin containing compound.

42. The process according to Claim 34 or 35, wherein said enhancing material is a tungsten containing compound.

43. The process according to Claim 10, wherein said enhancing material is a cobalt containing compound.

44. The process according to Claim 1, wherein said cathode includes an oxide or a hydroxide or contains the anions, selected from the group consisting of chalcogenide, chromate, molybdate, silicate, malonate, succinate, tartrate, selenate, sulfate, sulfite, halide, nitrate, bromate, chlorate, perchlorate, acetate, oxalate, carbonate, benzoate, hypochlorite, chlorite, dithionate, formate, iodate, periodate, carbonates, acetates, acetylsalicylates, alumminates, aluminum hudrides, amides, antomonides,

arsenates, azides, benzoates, borates, bromides, carbides, chlorates, chlorides, chloroplatinates, chromates, citrates, fluorides, fluosilicates, fluosulfonates, gallium hydrides, gallium nitrides, germanates, hydrides, iodides, laurates, manganates, permanganates, molybdates, myristates, nitrates, nitrides, nitrites, oxalates, palmitates, phosphates, salicylates, selenides, silicates, silicides, stearates, sulfates, sulfides, sulfites, tartrates, thiocyanates, thionates, or tungstates.

45. The process according to Claim 1, wherein said cathode includes a cation, selected from the group consisting of the alkali cations, H , the alkali earth cations, transition metal cations, or containing cations of group III, group IV and group V or ammonium or organic ammonium cations, or a lithium cation and a material capable of incorporating the lithium ions, consisting of a carbon based material, or a tin based material, or a lithium intercalating material.

46. The process substantially as described in the specifications and in any one of Claims 1 to 45.

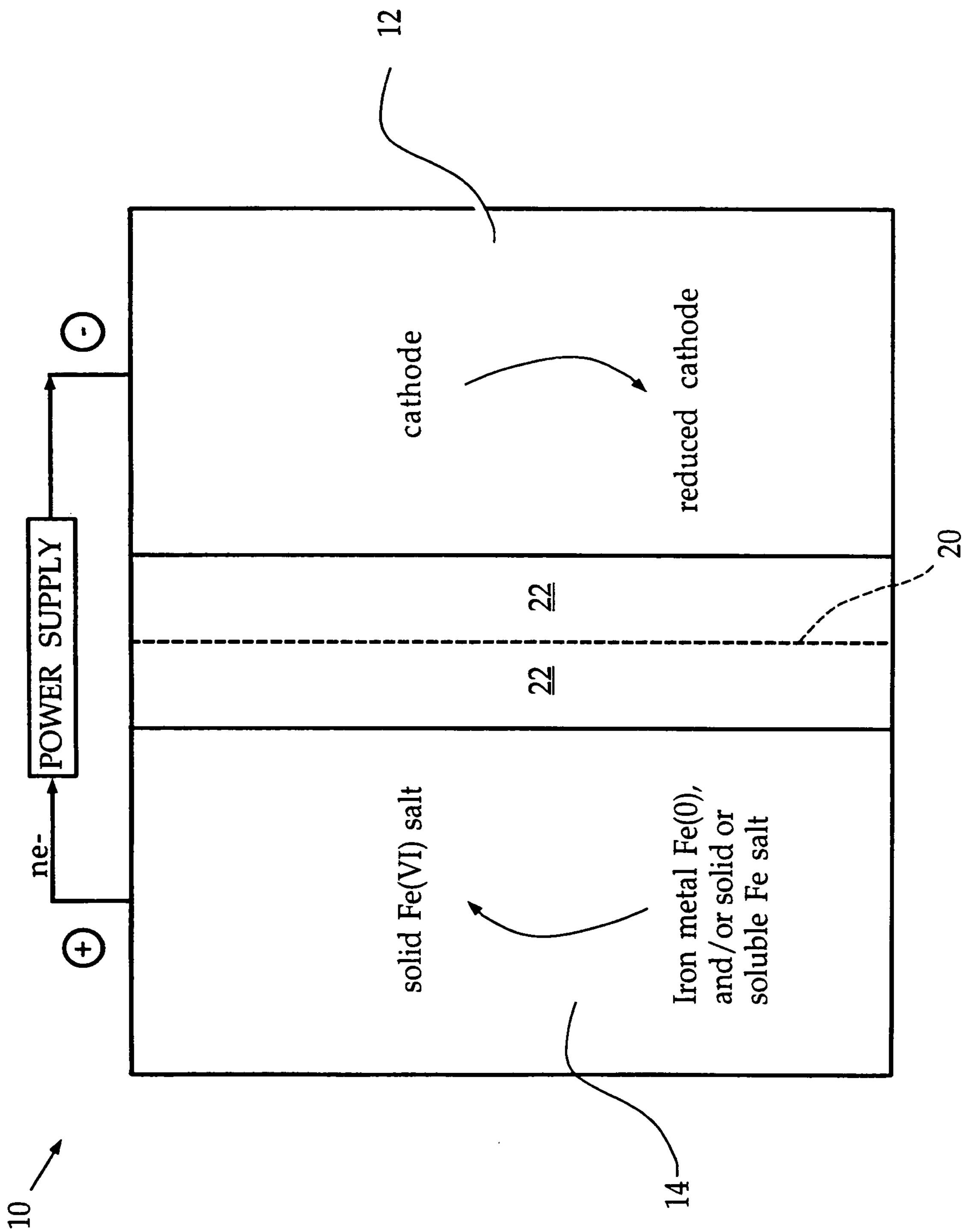
12
cathode
reduced cathode
POWER SUPPLY
ne-
20
22
22
solid Fe(VI) salt
Iron metal Fe(0), and/or solid or soluble Fe salt
14
10

FIG. 1

INTERNATIONAL SEARCH REPORT

International Application No
PCT/IL 00/00588

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C25B1/28 H01M4/58

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C25B H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 217 584 A (J. PAUL DEININGER) 8 June 1993 (1993-06-08) column 15 -column 18; example 3 ---	1,2,5,9, 10,22, 23,27,29
X	WO 98 50970 A (CHEMERGY LTD) 12 November 1998 (1998-11-12) see whole document -----	1,2, 5-12, 15-17, 20-35,37

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

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Date of the actual completion of the international search	Date of mailing of the international search report
26 February 2001	06/03/2001

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Groseiller, P

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/IL 00/00588

Patent document cited in search report		Publication date	Patent family member(s)			Publication date
US 5217584	A	08-06-1993	AU	8919991	A	20-05-1992
			WO	9207114	A	30-04-1992
WO 9850970	A	12-11-1998	AU	729009	B	25-01-2001
			AU	7077298	A	27-11-1998
			BR	9809231	A	31-10-2000
			CN	1260069	T	12-07-2000
			EP	0974169	A	26-01-2000
			PL	336666	A	03-07-2000
			US	6033343	A	07-03-2000

ELECTROLYTIC PRODUCTION OF SOLID Fe(VI) SALTS

The present invention relates to the novel preparation of Fe(VI) salts. More particularly the invention relates to a method for the preparation of Fe(VI) salts, also known as Super-iron or ferrates, based on direct electrolytic synthesis into the solid-phase.

BACKGROUND OF THE INVENTION

There is an ongoing need for providing chemical oxidizing agents which are low-cost and are acceptable by the environment for a wide variety of applications including improved batteries, chemical synthesis and water purification. For example, for batteries, prima facie, salts containing iron in the +6 valence state, hereafter called Fe(VI) which are capable of multiple electron reduction, or multiple ion intercalation, would be capable to provide a higher cathode storage capacity.

Fe(VI) salts such as sodium, potassium and calcium/sodium ferrates, have been previously electrochemically formed by anodic dissolution which forms a solution containing dissolved Fe(VI). This has been reported by J. P. Deininger et al. (U.S. Patents 4451338, 4435257 and 435256), and more recently by Devir et al. (J. App. Electrochem. 26, 823-827, 1996) and by Bouzek et al (Electrochem. Commun. 1, 370-374, 1999). Following this, solid Fe(VI) salts may be recovered by precipitation as a solid adduct.

Electrochemical synthesis by anodic dissolution has several unattractive features. These include that Fe(VI) is produced only in a highly dilute, and hence less useful, form.

DETAILED DESCRIPTION OF THE INVENTION

The novel battery according to the present invention is based on Fe(VI) (hereafter also called "super iron") half cell in contact with a cathode half cell through an electrically neutral ionic conductor. The preparation of this solid super iron salt is based on the electrolytic oxidation of a half cell containing at least 1% by weight of iron in its 0 (metal or Fe(0)), and/or +2 (Fe(II)), and/or +3 (Fe(III) valence state. The electrically neutral ionic conductor has a Fe(VI) salt dissolving capacity less than the quantity of prepared Fe(VI) salt. This undissolved prepared Fe(VI) salt is in the solid phase. This overcomes the unattractive features of anodic dissolution synthesis, and is capable of producing more concentrated Fe(VI), which avoids solution phase Fe(VI) decomposition losses during synthesis, and which is formed without the need for precipitating agents.

The solid Fe(VI) salt is illustrated by $MFeO_4$, M being an alkali earth cation. Other typical examples includes a cation, selected from the alkali cations, in the form M_2FeO_4, or from the group consisting of the transition metal cations, or containing, cations of group III, group IV and group V elements, with charge +z, and of the form $M_{2/z}FeO_4$. Similarly Fe(VI) salts in addition to oxygen, can contain hydroxide and/or other anions, X, of charge -y, and of the generalized form: $M_{2/z}FeX_{8/y}$. The anion, X, include, but are not limited to: hydroxides, acetates, acetylsalicylates, alumminates, aluminum hydrides, amides, antomonides, arsenates, azides, benzoates, borates, bromides, bromates, carbides, carbonates, chlorates, perchlorates, chlorides, hypochlorites, chlorites, dithiones, chloroplatinates, chromates, citrates, fluorides,

The electrically neutral ionic conductor utilized in the battery according to the present invention, comprises a medium that can support current density during battery discharge. Typical representative ionic conductor is an aqueous solutions preferably containing a high concentration of a hydroxide such as KOH.

In typical embodiments, the electrically neutral ionic conductor comprises common ionic conductor materials used in electrolytic processes which include, but are not limited to an aqueous solution, a non-aqueous solution, a conductive polymer, a solid ionic conductor and a molten salt.

According to another embodiment, the invention provides means to impede transfer of chemically reactive species, or prevent electric contact between the anode and Fe(VI) salt cathode. Said means includes, but is not limited to a membrane a ceramic frit, or agar solution, positioned to separate said half cells or a non-conductive separator configured with open channels, grids or pores.

A material addition, from 0.1 to 50%, and in the preferred range from 1 to 10%, to the electrically neutral ionic conductor, or to the iron in its 0, +2 or +3 valence state, can modify the quantity and the physical, chemical and electrochemical characteristics of the Fe(VI) salt which will be formed, and or modify the voltage and coulombic efficiency of the Fe(VI) electrolytic formation process. A material addition of a barium compound, can be used to decrease the solubility of Fe(VI) salts to improve the quantity of Fe(VI) salt produced. Barium additions include, but are not limited to, barium(II) compounds, as illustrated by BaX_2 and BaY_3, where X and Y are anions as previously described.

Table 1. Examples of the dissolving capacity of various aqueous and non-aqueous solutions for Fe(VI) salts, as expressed by the solution solubility; where for a cell containing a volume, V, of solution, the dissolving capacity is V x the Solubility. $LiClO_4$, LiTFB, LiTFMS refers to 1M, molar. in lithium perchlorate, or 1M in lithium tetrafluoroborate, or 1M lithium tetrafluoromethane sulfonate.

Solution	Salt	S, Solubility
water	$BaFeO_4$	$<< 10^{-5}$ M
aqueous 0.2 M $Ba(OH)_2$	$BaFeO_4$	$<< 10^{-5}$ M
aq. 5 M KOH & satd $Ba(OH)_2$	$BaFeO_4$	$< 2x10^{-4}$ M
aq. 5 M KOH & satd $Ba(OH)_2$	K_2FeO_4	$< 2x10^{-4}$ M
aq. 5 M KOH	$BaFeO_4$	$5x10^{-4}$ M
aq. 5 M KOH	K_2FeO_4 + $Ba(OH)_2$	$5x10^{-4}$ M
aq. 5 M KOH	K_2FeO_4	$7x10^{-2}$ M
aq. 5 M LiOH	K_2FeO_4	$9x10^{-1}$ M
aq. 5 M NaOH	K_2FeO_4	1.4 M
aq. 5 M CsOH	K_2FeO_4	$3.5x10^{-2}$ M
aq. 10 M NaOH	K_2FeO_4	$5x10^{-1}$ M
aq. 10 M KOH	K_2FeO_4	$1x10^{-2}$ M
aq. satd. KOH	K_2FeO_4	$2x10^{-3}$ M
acetonitrile (ACN)	$BaFeO_4$, K_2FeO_4	$<< 10^{-5}$ M
ACN $LiClO_4$, LiTFB, LiTFMS	$BaFeO_4$, K_2FeO_4	$<< 10^{-5}$ M
Propylene carbonate (PC)	$BaFeO_4$, K_2FeO_4	$<< 10^{-5}$ M
PC $LiClO_4$, LiTFB, LiTFMS	$BaFeO_4$, K_2FeO_4	$<< 10^{-5}$ M
acetone	$BaFeO_4$, K_2FeO_4	$<< 10^{-5}$ M
hexane	$BaFeO_4$, K_2FeO_4	$<< 10^{-5}$ M
chloroform	$BaFeO_4$, K_2FeO_4	$<< 10^{-5}$ M
sulfonane	$BaFeO_4$, K_2FeO_4	$<< 10^{-5}$ M
1,4 - dioxane	$BaFeO_4$, K_2FeO_4	$<< 10^{-5}$ M
ethylene carbonate (EC)	$BaFeO_4$, K_2FeO_4	$<< 10^{-5}$ M
EC + 0.5 M $LiClO_4$	$BaFeO_4$, K_2FeO_4	$<< 10^{-5}$ M
γ-butyrlactone (BLA)	$BaFeO_4$, K_2FeO_4	$<< 10^{-5}$ M
BLA + 0.5 M $LiClO_4$	$BaFeO_4$, K_2FeO_4	$<< 10^{-5}$ M
tetrahyrofuran (THF)	$BaFeO_4$, K_2FeO_4	$<< 10^{-5}$ M
THF + 1 M $LiClO_4$	$BaFeO_4$, K_2FeO_4	$<< 10^{-5}$ M
Dimethoxyethane (DME)	$BaFeO_4$, K_2FeO_4	$<< 10^{-5}$ M
DME $LiClO_4$, LiTFB, LiTFMS	$BaFeO_4$, K_2FeO_4	$<< 10^{-5}$ M
Dimethylformamide (DMF)	$BaFeO_4$, K_2FeO_4	$<< 10^{-5}$ M
DMF + 1 M LiTFMS	$BaFeO_4$, K_2FeO_4	$<< 10^{-5}$ M
Dimethylsulfoxide (DMSO)	$BaFeO_4$, K_2FeO_4	$<< 10^{-5}$ M
DMSO + 1 M $LiClO_4$	$BaFeO_4$, K_2FeO_4	$<< 10^{-5}$ M

Example 2

An experiment was carried out, the object being to produce electrolytic solid Fe(VI) salt using an electrochemical cell as diagrammatically illustrated in Fig. 1. The electrochemical cell configuration consisted of a 2 cm diameter button cell comprised of an upper (cathode) section, pressing onto a mid (separator) section, pressing onto a lower (anode) section.

The upper section of the electrochemical cell configuration comprises an upper inverted metal dish plate (the cathode cap) pressing onto a metal washer type spring, which presses onto a metal screen (the cathode collector), pressing onto a metal hydride material removed from a discharge commercial metal hydride battery. The quantity of metal hydride is determined to be in coulombic excess of the iron starting material, as determined in accord with equations 2-5. The mid section consists of a separator material removed from a commercial metal hydride battery and is surrounded by a PTFE washer to prevent direct contact or electrical shorting of the upper and lower section. Various electrolytes as electrically neutral ionic conductors, in various amounts, were tested, and are added to the separator and anode material. The lower section consists of a pressed mixed powder pressed into a bottom metal dish plate. Various cells were formed with powders containing a variety of iron materials in the Fe(0), Fe(II), or Fe(III) valence state, as well as various tested additives and added conductors.

An oxidizing current was applied to the anode using a constant current power supply connected for a fixed time to the upper and lower plates of the electrochemical cell

removal from an opened AA cylindrical Ni-Cd battery, were used. In one case, the starting material was 125 mAh of $BaO \cdot 1.5Fe_2O_3$, prepared in accord with equation 10. In addition, the starting anode mix contains a 1:2 molar ratio of $Ba(OH)_2 \cdot 8H_2O$ to $BaO \cdot 1.5Fe_2O_3$, and 25% by weight of carbon black. The anode mix was pressed at 1000 kg into the anode compartment. Then, 0.37 grams of 13.5 M KOH electrolyte was soaked on the anode mix for 12 hours, and subsequently the separator and cathode were pressed into the cell. A 10 mA current was applied to the anode, through the cell for 50 hours. The anode material was removed, and the product contained 82.9% conversion of Fe(III) into solid Fe(VI), such as $BaFeO_4$, as determined by chromite analysis.

In a second case in the 4 cm diameter synthesis cell, the anode mix contained 50 mAh of $2BaO \cdot Fe_2O_3$. The $2BaO \cdot Fe_2O_3$ was prepared from $2BaCO_3$ and Fe_2O_3, pressing the mixture at 1000 kg, and heating in air at 900°C for 24 hours. The anode mix also contained 25% by weight KOH, 25% carbon black, as well as 1% $Ba(OH)_2 \cdot 8H_2O$ and 2% KIO_4. The anode mix was pressed at 1000 kg into the anode compartment. Then, 0.32 grams of 13.5 M KOH electrolyte was soaked on the anode mix for 12 hours, and subsequently the separator and cathode were pressed into the cell. A 50 mA current was applied to the anode, through the cell for 3 hours. The anode material was removed, and the product contained 75.2% conversion of Fe(III) into solid Fe(VI), as determined by chromite analysis.

CLAIMS:

1. A process for preparing Fe(VI) salts which comprising two half-cells which are in an electrochemical contact with one another through an electrically neutral ionic conductor, wherein one of said half-cells comprises a cathode and the other half-cell comprises at least 1% of weight of an iron containing material, wherein a power supply is used to oxidize the iron containing material to a solid Fe(VI) salt.

2. The process according to Claim 1, wherein said iron containing material is a solid or dissolved Fe(III) salt.

3. The process according to Claim 1, wherein said iron containing material is a solid or dissolved Fe(II) salt.

4. The process according to Claim 1, wherein said iron containing material is iron metal, Fe(0).

5. The process according to Claim 2 or 3, wherein said salt is an oxide or a hydroxide or contains the anions, selected from the group consisting of acetates, acetylsalicylates, alumminates, aluminum hudrides, amides, antomonides, arsenates, azides, benzoates, borates, bromides, bromates, carbides, carbonates, chlorates, perchlorates, chlorides, hypochlorites, chlorites, dithionate, chloroplatinates, chromates, citrates, fluorides, fluosilicates, fluosulfonates, formates, gallium hydrides, gallium nitrides, germanates, hydrides, iodates, iodides, periodate, laurates, manganates, malonates, permanganates, molybdates, myristates, nitrates, nitrides, nitrites, oxalates, palmitates, phosphates, salicylates, selenates, selenides, silicates, silicides, stearates, succinates, sulfates, sulfides, sulfites, tartrates, thiocyanates, thionates, tungstates, halides, or chalcogenides.

6. The process according to Claim 2 or 3, wherein said salt includes a cation, selected from the group consisting of the alkali cations, H^+, the alkali earth cations, transition metal cations, or containing cations of group III, group IV and group V or ammonium or organic ammonium cations.

7. The process according to Claims 1 to 4, wherein said electrically neutral ionic conductor is an aqueous solution.

8. The process according to Claims 1 to 4, wherein said electrically neutral ionic conductor is a nonaqueous solution.

9. The process according to Claims 1 to 4, wherein said electrically neutral ionic conductor is a conductive polymer.

10. The process according to Claims 1 or 2, wherein said electrically neutral ionic conductor is a solid ionic conductor.

11. The process according to Claims 1 to 4, wherein said electrically neutral ionic conductor is a molten salt.

12. The process according to Claims 7 to 11, wherein said neutral ionic conductor contains a dissolved salt.

13. The process according to Claims 7 to 9, wherein said neutral ionic conductor contains a dissolved liquid.

14. The process according to Claim 13, wherein said dissolved liquid is an organic solvent.

15. The process according to Claims 7-11, wherein said neutral ionic conductor contains the concentration of up to saturation in hydroxide ions.

16. The process according to Claim 12, wherein said dissolved salt is an iron salt in a concentration of up to saturation.

17. The process according to Claim 16, wherein said iron salt an Fe(VI) salt.

18. The process according to Claim 16, wherein said iron salt an Fe(III) salt.

19. The process according to Claim 16, wherein said iron salt an Fe(II) salt.

20. The process according to Claim 12, wherein said dissolved salt is an oxide or a hydroxide or contains the anions, selected from the group consisting of acetates, acetylsalicylates, alumminates, aluminum hudrides, amides, antomonides, arsenates, azides, benzoates, borates, bromides, bromates, carbides, carbonates, chlorates, perchlorates, chlorides, hypochlorites, chlorites, dithionate, chloroplatinates, chromates, citrates, fluorides, fluosilicates, fluosulfonates, formates, gallium hydrides, gallium nitrides, germanates, hydrides, iodates, iodides, periodate, laurates, manganates, malonates, permanganates, molybdates, myristates, nitrates, nitrides, nitrites, oxalates, palmitates, phosphates, salicylates, selenates, selenides, silicates, silicides, stearates, succinates, sulfates, sulfides, sulfites, tartrates, thiocyanates, thionates, tungstates, halides, or chalcogenides.

21. The process according to Claim 12, wherein said dissolved salt includes a cation, selected from the group consisting of the alkali cations, H^+, the alkali earth cations, transition metal cations, or containing cations of group III, group IV and group V or ammonium or organic ammonium cations.

22. The process according to Claims 1 to 4, further characterized in that said iron containing material is in contact with a conductive material.

23. The process according to Claim 22, wherein said conductive material is selected from graphite, carbon black and a metal.

24. The process according to Claim 22, wherein said iron containing material-conductive material comprises a mixed pressed powder.

25. The process according to Claim 22, wherein said iron containing material-conductive material comprises a planar surface or a wire.

26. The process according to Claim 22, wherein said iron containing material-conductive material comprises a porous substrate or grid.

27. The process according to Claims 1 to 4 further comprising means to impede transfer of chemically reactive species between said anode and said other half cell.

28. The process according to Claim 27, wherein said means is a non conductive separator configured with open channels, grids or pores.

29. The process according to Claim 26 in which said means to impede transfer of chemically reactive species comprises a membrane positioned to separate said half cells.

30. The process according to Claim 1, wherein said cathode includes a non metal inorganic salt capable of being reduced.

31. The process according to Claim 1, wherein said cathode includes a metal inorganic salt capable of being reduced.

32. The process according to Claim 1, wherein said cathode includes an organic compound capable of being reduced.

33. The process according to Claim 32, wherein said organic compound is selected from the group consisting of aromatic and non-aromatic compounds.

34. The process according to Claims 1, further characterized in that said neutral ionic conductor contains an added enhancing material to modify the Fe(VI) salt production.

35. The process according to Claims 1 to 4, further characterized in that said iron containing material contains an added enhancing material to modify the Fe(VI) salt production.

36. The process according to Claim 34 or 35, wherein said enhancing material is a Ba(II) compounds.

37. The process according to Claim 34 or 35, wherein said enhancing material is an oxygen containing compound, such as an oxide or hydroxide compound.

38. The process according to Claim 34 or 35, wherein said enhancing material is an indium containing compound.

39. The battery according to Claim 1, wherein said enhancing material is a manganese containing compound.

40. The process according to Claim 10, wherein said charging voltage altering material, is a lithium containing compound.

41. The process according to Claim 34 or 35, wherein said enhancing material is a tin containing compound.

42. The process according to Claim 34 or 35, wherein said enhancing material is a tungsten containing compound.

43. The process according to Claim 10, wherein said enhancing material is a cobalt containing compound.

44. The process according to Claim 1, wherein said cathode includes an oxide or a hydroxide or contains the anions, selected from the group consisting of chalcogenide, chromate, molybdate, silicate, malonate, succinate, tartrate, selenate, sulfate, sulfite, halide, nitrate, bromate, chlorate, perchlorate, acetate, oxalate, carbonate, benzoate, hypochlorite, chlorite, dithionate, formate, iodate, periodate, carbonates, acetates, acetylsalicylates, alumminates, aluminum hudrides, amides, antomonides,

arsenates, azides, benzoates, borates, bromides, carbides, chlorates, chlorides, chloroplatinates, chromates, citrates, fluorides, fluosilicates, fluosulfonates, gallium hydrides, gallium nitrides, germanates, hydrides, iodides, laurates, manganates, permanganates, molybdates, myristates, nitrates, nitrides, nitrites, oxalates, palmitates, phosphates, salicylates, selenides, silicates, silicides, stearates, sulfates, sulfides, sulfites, tartrates, thiocyanates, thionates, or tungstates.

45. The process according to Claim 1, wherein said cathode includes a cation, selected from the group consisting of the alkali cations, H , the alkali earth cations, transition metal cations, or containing cations of group III, group IV and group V or ammonium or organic ammonium cations, or a lithium cation and a material capable of incorporating the lithium ions, consisting of a carbon based material, or a tin based material, or a lithium intercalating material.

46. The process substantially as described in the specifications and in any one of Claims 1 to 45.